

MiniSipper: A new in situ water sampler for high-resolution, long-duration acid mine drainage monitoring☆

Thomas P. Chapin □, Andrew S. Todd ¹

U.S. Geological Survey, Box 25046, MS 964D, Denver Federal Center, Denver, CO 802225, USA

HIGHLIGHTS

- Collects 250 five milliliter in situ acidified samples, operates for >8 months in freezing conditions.
- Captures details of seasonal and episodic events.
- Excellent agreement with EPA and USGS hand collected samples.
- Better estimates of toxic metal loading from acid mine drainage sources.
- Low cost, portable, and useful for locations that are difficult to sample with traditional methods.

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abstract

Abandoned hard-rock mines can be a significant source of acid mine drainage (AMD) and toxic metal pollution to watersheds. In Colorado, USA, abandoned mines are often located in remote, high elevation areas that are snowbound for 7–8 months of the year. The difficulty in accessing these remote sites, especially during winter, creates challenging water sampling problems and major hydrologic and toxic metal loading events are often under sampled. Currently available automated water samplers are not well suited for sampling remote snowbound areas so the U.S. Geological Survey (USGS) has developed a new water sampler, the MiniSipper, to provide long-duration, high-resolution water sampling in remote areas. The MiniSipper is a small, portable sampler that uses gas bubbles to separate up to 250 five milliliter acidified samples in a long tubing coil. The MiniSipper operates for over 8 months unattended in water under snow/ice, reduces field work costs, and greatly increases sampling resolution, especially during inaccessible times. MiniSippers were deployed in support of an U.S. Environmental Protection Agency (EPA) project evaluating acid mine drainage inputs from the Pennsylvania Mine to the Snake River watershed in Summit County, CO, USA. MiniSipper metal results agree within 10% of EPA-USGS hand collected grab sample results. Our high-resolution results reveal very strong correlations ($R^2 > 0.9$) between potentially toxic metals (Cd, Cu, and Zn) and specific conductivity at the Pennsylvania Mine site. The large number of samples collected by the MiniSipper over the entire water year provides a detailed look at the effects of major hydrologic events such as snowmelt runoff and rainstorms on metal loading from the Pennsylvania Mine. MiniSipper results will help guide EPA sampling strategy and remediation efforts in the Snake River watershed.

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1. Introduction

1.1. Acid mine waters

Acid mine drainage (AMD) from active or abandoned mines is considered one of the greatest threats to water quality around the world (Johnson and Hallberg, 2005; Nordstrom, 2011). Mining of

metal or coal deposits exposes sulfide bearing minerals to water and oxygen which generate acidic conditions and liberate potentially toxic elements (Nordstrom and Alpers, 1999). In the western USA, more than 160,000 abandoned mine sites have been identified and over 33,000 sites (~20%) are known to degrade the environment (US GAO, 2011). Many of the acid mine drainage sites in the western USA and around the world are located in remote high elevation or high latitude watersheds where snowmelt runoff is the dominant hydrologic process (Herbert, 2006; Kimball et al., 2010; Sondergaard, et al., 2012). Water sampling at these remote, high elevation or high latitude sites is usually limited to a few hand collected grab samples during the accessible summer period and this low-resolution water sampling rarely captures the details of major toxic metal loading

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□ Corresponding author. Tel.: +1 303 236 5795; fax: +1 303 236 5795.

E-mail addresses: tchapin@usgs.gov (T.P. Chapin), atodd@usgs.gov (A.S. Todd).

¹ Tel.: +1 303 236 1426; fax: +1 303 236 5795.

events such as snowmelt runoff or large rainstorms. (He et al., 1997; Gray, 1998; Sullivan and Drever, 2001; Herbert, 2006; Davies et al., 2011; Nimick et al., 2011; Sondergaard et al., 2012).

The abandoned Pennsylvania Mine has been identified as the largest point source of toxic metals to the Snake River Watershed in Summit County, Colorado, USA (Fig. 1, CDPHE, 2008). The Snake River watershed has been extensively studied but most of the data was collected during the 4 month accessible summer period (McKnight and Bencala, 1990; McKnight et al., 1999; Sullivan and Drever, 2001; Fey et al., 2002; Todd et al., 2003, 2007; Church et al., 2009). Local, State and Federal agencies are examining clean up options for the Pennsylvania Mine but their remediation designs are hampered by the limited amount of water quality data collected during major runoff events such as snowmelt runoff and large rainstorms. In order to better understand the effects of major runoff events at the Pennsylvania Mine, the EPA has contracted with the USGS to provide high-resolution water sampling at the Pennsylvania Mine over the entire water year to help guide EPA remediation efforts.

This report will discuss the development and application of the MiniSipper, a low-cost, in situ water sampler for long-duration, high-resolution environmental monitoring. MiniSipper technology collects water samples over the entire year, even in freezing conditions, and provides a detailed look at transient metal fluxes from the Pennsylvania Mine and their potential impact on the Snake River watershed.

1.2. Area description

The Snake River watershed is located on the western slope of the Continental Divide in Summit County, CO, USA (Fig. 1). The watershed lies within the Colorado mineral belt and the bedrock in this area contains disseminated pyrite and other metal sulfides (Lovering and Goddard, 1950). The Snake River watershed has a number of areas where natural rock weathering or abandoned mine sites mobilize high levels of potentially toxic metals such as cadmium (Cd), copper (Cu), lead (Pb), manganese (Mn), and zinc (Zn) (Neubert et al., 2011).

Elevations in the Snake River watershed range from 2800 to 4200 m and the annual hydrograph is dominated by snowmelt runoff in early summer. The Pennsylvania Mine is located at 3330 m elevation on Peru Creek, a major tributary of the Snake River (Fig. 1). The major sulfide minerals at the Pennsylvania Mine are pyrite, galena, sphalerite and chalcopyrite and the site was mined for gold, silver, lead, copper and zinc from the late 1870s through the 1940s (Lovering and Goddard, 1950).

Six mine levels (A–F) were tunneled at the Pennsylvania Mine with an estimated 80 km of underground workings (CDPHE, 2008). The mine site contains extensive waste rock piles and all the mine level portals have collapsed so there is no access to the underground

workings. The only significant surface water discharge at the Pennsylvania Mine flows from the collapsed Level F adit and this AMD flows over waste rock piles to Peru Creek (Fig. 1). Subsurface flow from the mine workings and waste rock piles also contributes AMD to Peru Creek but will not be addressed in this study. Peru Creek flows for 6 km until it joins with the Snake River. The Snake River then flows for 6 km to the ski resort town of Keystone and then another 6 km downstream to the Dillon Reservoir, a recreation area and municipal water supply for the city of Denver (Fig. 1).

The Snake River and Peru Creek were listed as impaired water bodies in 2008 due to elevated concentrations of cadmium, copper, lead, and zinc, and Peru Creek has an additional listing for manganese (CDPHE, 2008). The Level F adit outflow from the Pennsylvania Mine is considered the largest point source of toxic metals in the Snake River watershed and this site has been targeted for remediation efforts (CDPHE, 2008). Water quality in the Snake River is crucial for both summer and winter recreation in the area and changes in water use and/or cleaning up pollution sources could have a large impact on overall water quality (Todd et al., 2003).

1.3. Water sampling methods for acid mine drainage monitoring

Hand collected grab samples are the most common type of water sampling methodology used for remote sites. Grab sampling can be very labor intensive and expensive, with significant costs for personnel salary, field vehicles and equipment. Grab sampling provides a 'snapshot' of environmental conditions and this low temporal resolution sampling typically collects a few samples per year when the field site is easily accessible. Long-duration, high-resolution grab sampling in remote and/or snowbound areas is usually not feasible or affordable.

Currently available automated water samplers or diffusion based water samplers can provide long-duration sampling in remote areas but these sampling methods have many limitations. Diffusion based in situ samplers have been successfully used in acid mine drainage monitoring but these samplers only collect one time integrated sample per deployment and provide little information about transient hydrologic loading events such as snowmelt runoff or rain storms (Aguilar-Martinez et al., 2009; Balistrieri et al., 2012). Commercially available automated water samplers (e.g. Teledyne-Isco, Sigma, Sirco, etc.) are large, heavy (>50 kg with battery and samples), and typically collect twenty-four 500 or 1000 mL samples. Sample collection with these automated samplers is well established and these instruments can provide high resolution sampling for a few days or weeks but are not well suited for operation in freezing winter conditions or for long duration unattended sampling at remote sites (Fey et al., 2002; Kimball et al., 2010).

The USGS developed the MiniSipper to overcome the limitations of currently available water sampling technology and provide long duration, high resolution water sampling at low cost. MiniSipper technology takes advantage of recent advances in high sensitivity multi-element analytical instruments such as inductively coupled plasma mass spectrometry (ICP-MS) which have greatly reduced the sample volume required for analysis. MiniSipper sampling technology starts with the premise that small sample volumes (~5 mL) are sufficient for many studies and the instrumental challenge is how to reliably collect, separate and preserve these small volume water samples during long deployments.

2. Methods

2.1. MiniSipper general description

The basic MiniSipper concept is the automated in situ collection of small volume water samples and storage in a long sample coil. Water samples are preserved online with acid and samples are separated by

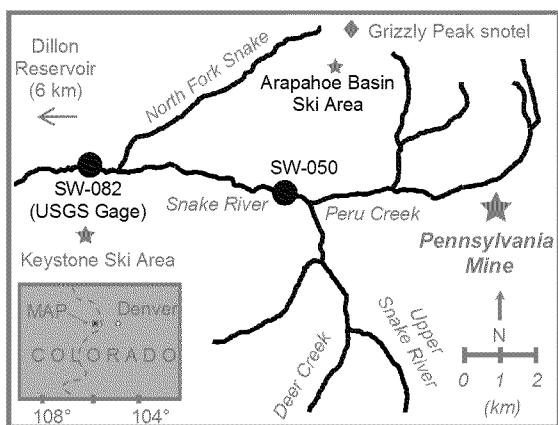


Fig. 1. Snake River watershed map.

inert gas bubbles, an effective separation technique first used in continuous flow chemical analyzers in the late 1950s (Skeggs, 1957). MiniSipper components are: 1) waterproof housing containing microcontroller, three solenoid micro-pumps, and rechargeable battery; 2) sample coil with 150 m of 3.2 mm OD by 1.6 mm ID high purity PFA (perfluoroalkoxy) tubing; 3) collapsible bag for the nitrogen N₂ gas bubble separator; and 4) a 50 mL coil of stabilizing reagent (HNO₃) (Fig. 2). The MiniSipper is relatively small (45 cm×30 cm) and light (<10 kg) which makes transport and deployment in remote or difficult to access locations much easier. The total cost for the MiniSipper instrumentation is approximately \$2000 (USD). A detailed description of MiniSipper development, construction and operation is presented in the Supplementary material section.

Sample, acid and bubble volumes and sampling interval are all user selectable and the sample coil has a capacity of 1250 mL. In typical operation, the MiniSipper injects a 5 mL water sample into the sample coil, injects 0.25 mL of high purity nitric acid to stabilize the water sample, and then injects a 0.5 mL gas bubble to create a separation barrier between the next sample. MiniSipper samples are filtered in situ with 10 µm ultra-high molecular weight polyethylene solvent filter. Over 250 five milliliter water samples can be loaded into the sample coil and total sample carryover is typically 5–10%.

MiniSippers are in situ instruments submerged at the sampling site. A metal stake is usually pounded into the stream bottom and the MiniSipper is secured to this stake. Large river rocks are placed on top of the MiniSipper to further anchor the instrument and provide concealment to decrease the risk of vandalism. MiniSippers were deployed at the Pennsylvania Mine Level F adit for 2–3 months during the more easily accessible summer period, sampling every 12–24 h. During over-winter deployments MiniSippers collected

samples weekly until early May when the sampling rate automatically changed to daily sampling during the snowmelt runoff period.

2.2. Sample processing and ICP-MS analysis

After recovery, the MiniSipper was returned to the laboratory and samples were sequentially pumped out of the sample coil and into 15 mL polyethylene centrifuge tubes and capped for later ICP-MS analysis. Sample weights and visual location of each N₂ separation bubble were recorded for each sample. Offloaded sample pH and conductivity were routinely checked during sample coil offload to verify in situ acidification during deployment.

Offloaded MiniSipper samples were diluted from 1:10 to 1:100 depending on expected metal concentrations and analyzed at USGS laboratories in Denver, CO, USA for 57 elements from lithium to uranium on a Perkin Elmer Elan 6000 Dynamic Reaction Cell Inductively Coupled Plasma Mass Spectrometer (DRC-ICP-MS) with AS-90 autosampler (Lamothe et al., 2002). During ICP-MS analysis, the diluted MiniSipper sample was mixed online with an acidified internal standard containing 3 elements (Li-6, In-115, Ir-193) to correct for variations in instrument performance following standard USGS methods (Taggart, 2002). USGS Standard Reference Materials for major ions (USGS M-187), trace metals (USGS T-131), and low concentration multi-element standards were analyzed every 30–40 samples during ICP-MS runs to further monitor accuracy and performance. Detection limits for the USGS ICP-MS analyses were generally below 1 µg/L (Lamothe et al., 2002).

2.3. Pennsylvania mine conductivity, depth, flow and weather data

Conductivity loggers (Instrumentation Northwest CT2X, Onset Hobo-U24) were co-deployed with MiniSippers and recorded specific conductivity and temperature at 15–30 minute intervals. Water depth at the Pennsylvania Mine Level F outflow was monitored during 2010 with either a vented In-Situ Level Troll 500 or unvented In-Situ Level Troll 100. Barometric pressure data for unvented depth corrections and rainfall data were collected by a Spectrum WatchDog 200 weather station located at the Pennsylvania Mine site during the summer months and from a weather station in the nearby town of Dillon during the rest of the year (<http://www.wunderground.com/weatherstation/WXDailyHistory.asp?ID=KCODILLO>). Depth and flow data from the Pennsylvania Mine were not available after 2010 due to equipment failures and limited availability of instrumentation. Snow accumulation and additional precipitation data were obtained from the Grizzly Peak SNOTEL (snowpack telemetry) site (#505) located approximately 6 km from the Pennsylvania Mine (<http://www.wcc.nrcs.usda.gov/nwcc/site?sitenum=505&state=co>). Pennsylvania Mine Level F outflow runs through a 5 cm Parshall weir and depth measurements were converted to flow estimates with the manufacturer's weir rating curve.

2.4. EPA and USGS grab sample data and Snake River flow

EPA personnel collected grab samples at the Pennsylvania Mine site every 1 to 3 months from 2008 to 2011 (n = 20). Summer access required 4WD vehicles while winter sample collection required snowmobile travel to the site and digging through up to 3 m of snow to reach the outflow from the Pennsylvania Mine. Standard EPA grab sample collection methods for total metals, 0.45 µm filtered metals, pH and conductivity were used (EPA Method 1669, 1996). EPA water samples were analyzed independently by the EPA lab in Golden, CO using standard EPA methods for ICP-MS analysis (EPA Method 200.8, 1994). USGS personnel also collected 8 grab samples at the Pennsylvania Mine from 2008 to 2011 and the USGS grab samples were analyzed at the USGS in Denver, CO by ICP-MS techniques discussed previously.

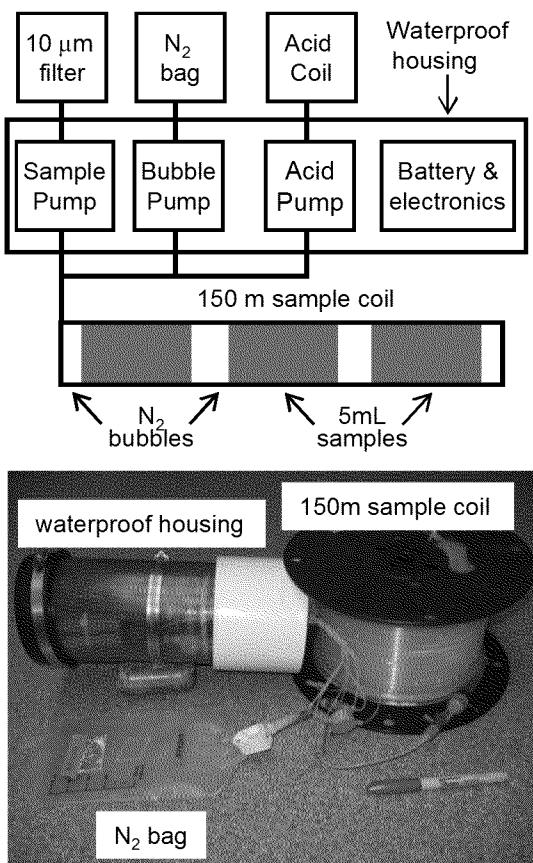


Fig. 2. MiniSipper in situ water sampler. Instrument collects 250 five milliliter samples and can be deployed for over 8 months at a time.

Snake River flow data were obtained from the USGS and Colorado Division of Water Resources (CDWR) gage sites co-located at water sampling site SW-082 in the town of Keystone, CO (Fig. 1, USGS gage site 09047500 and CDWR gage site SNAKEYCO). The North Fork of the Snake River joins the Snake River upstream of site SW-082 and contributes about 35% of the flow observed at SW-082 (Fig. 1, CDPHE, 2008). Site SW-050 is located 6 km upstream and flow at the site is estimated to be 0.63 of the flow at SW-082 (CDPHE, 2008). EPA grab sample metal data ($0.45\text{ }\mu\text{m}$ filtered, unpublished) from the two Snake River water sampling sites, SW-050 and SW-082, were used for metal loading calculations in Tables 1 and 2.

3. Results

3.1. Snake River flow and Pennsylvania Mine flow, specific conductivity and precipitation

The Snake River hydrograph at SW-082 in the town of Keystone, CO was dominated by snowmelt runoff with peak flows over $1300\text{ m}^3/\text{min}$ during maximal snowmelt runoff in June (Fig. 3b). By late summer, stream flow had returned to baseline levels ($\sim 15\text{ m}^3/\text{min}$) and flow remained low during winter until the next snowmelt runoff peak in June (Fig. 3b). Large summer rainstorms increased flow for some years (e.g. 2010) but were not observed every year (Fig. 3b). The large annual changes in peak flow runoff at SW-082 were related to changes in annual snowpack depth and precipitation (both snow and rain). Total annual precipitation (snow + rain from Oct 1–Sept 30) measured at the Grizzly Peak SNOTEL site, was 82 cm for 2009, 66 cm for a dry 2010, and 113 cm for a wet 2011. Maximum snowpack depths showed the same pattern with snowpack depths of 198 cm for 2009, 132 cm for a dry 2010, and 237 cm for a wet 2011 (Fig. 3b).

The water flowing out of Pennsylvania Mine Level F adit displayed a pronounced seasonal signal in many water quality parameters. Flow data from the Pennsylvania Mine adit was limited to 2010 but ranged from a low of $0.18\text{ m}^3/\text{min}$ during the low flow winter period to a high of $0.66\text{ m}^3/\text{min}$ during the snowmelt runoff in June 2010 (Fig. 3a). Specific conductivity from the Pennsylvania Mine showed a consistent annual pattern with lowest values during the low flow winter period (1.4 mS/cm) and highest values up to 2.5 mS/cm during the snowmelt runoff events (Fig. 3a). Conductivity changes were smooth and did not show significant diel cycling or rapid changes on sub-daily timescales (Fig. 3a). Temperature ranged from 2.4 to $3\text{ }^\circ\text{C}$ and was the only measured water parameter that did not display a large seasonal signal (not shown). Pennsylvania mine waters also showed a seasonal pH signal with highest values ($\text{pH }4.5\text{--}5.5$) during the low flow winter period and lowest values ($\text{pH }3$) during the

snowmelt runoff and summer period (Fig. 3a). Large summer rainstorms in 2010 lead to increases in flow and specific conductivity at the Pennsylvania Mine with peak flow and conductivity values close to the maximal values observed during June snowmelt runoff (Fig. 3a). Late summer high conductivity events at the Pennsylvania Mine were not observed every year (e.g. 2009, a wet 2011, Fig. 3a).

3.2. Pennsylvania Mine metal results

MiniSippers have been deployed at the Pennsylvania Mine Level F adit almost continuously since late 2008 and collected 750 water samples during that time. We have MiniSipper metal data for over 40 elements but our discussion will focus on the metals for which the Snake River and Peru Creek have historically exceeded water quality standards (Al, Cd, Cu, Mn, Pb, and Zn). Fig. 4 shows MiniSipper results in red for Al, Cd, Cu, Mn, Pb, and Zn and specific conductivity from 2008 to 2011 ($n = 750$). Large blue symbols in Fig. 4 are EPA and USGS $0.45\text{ }\mu\text{m}$ filtered grab samples collected and analyzed independently of the MiniSipper samples ($n = 28$).

The Pennsylvania Mine site had the lowest metal concentrations during the low flow winter period and the highest metal concentrations during runoff events (Fig. 4). During snowmelt runoff, metal concentrations at the Pennsylvania Mine adit increased 2–15 times over late winter low flow metal concentrations. Mn and Zn concentrations were high year round and ranged from a low of $30\text{--}40\text{ mg/L}$ to a high of $\sim 80\text{ mg/L}$ (Fig. 4). Cadmium concentrations ranged from a low of 0.1 to a high of 0.35 mg/L while Pb concentrations ranged from a low of 0.05 to a high of 0.2 mg/L . Aluminum and copper showed the greatest relative annual change with aluminum ranging from a winter low of 9 mg/L to a high of 64 mg/L during runoff events while copper ranged from a winter low of 1 mg/L to a high of 19 mg/L during runoff events (Fig. 4). After peak snowmelt runoff and peak metal concentrations in mid-June, metal concentrations at the Pennsylvania mine gradually declined over the next 6 months to low flow winter (baseline) metal concentrations (Fig. 4). The gradual decrease in metal concentrations after snowmelt runoff could be interrupted if large summer thunderstorms lead to a second metal concentration and conductivity peak as observed in 2010, but not observed in 2009 or 2011 (Fig. 4).

Most metals were highly correlated with conductivity at the Pennsylvania Mine (Fig. 5). Highest correlations were observed for Cd, Cu and Zn ($R^2 > 0.9$) while slightly lower correlations were observed for Mn and Pb and sulfate (Fig. 5). Sulfate correlations with conductivity were lower than expected due to problems with the sulfate standards and calibrations used in ICP-MS analyses. Major cations (Na, Mg, and Ca) were not well correlated with conductivity ($R^2 < 0.2$, Fig. 5).

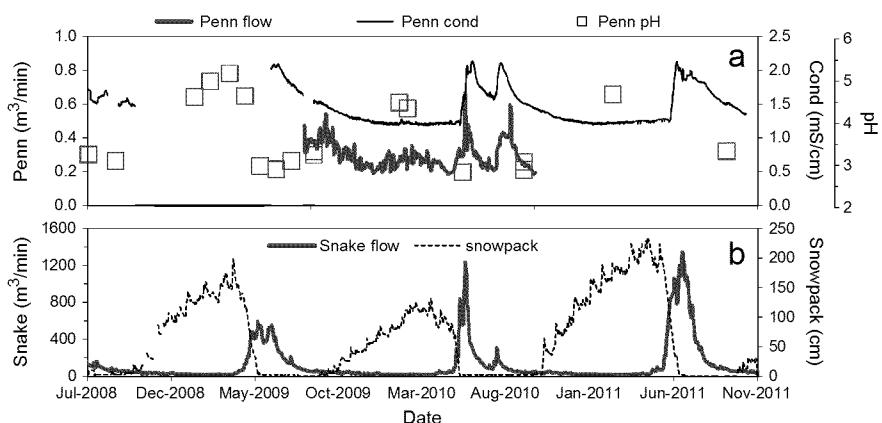


Fig. 3. Pennsylvania Mine flow, pH and conductivity (a) and Grizzly Peak snowpack and Snake River flow from 2008 to 2011 (b).

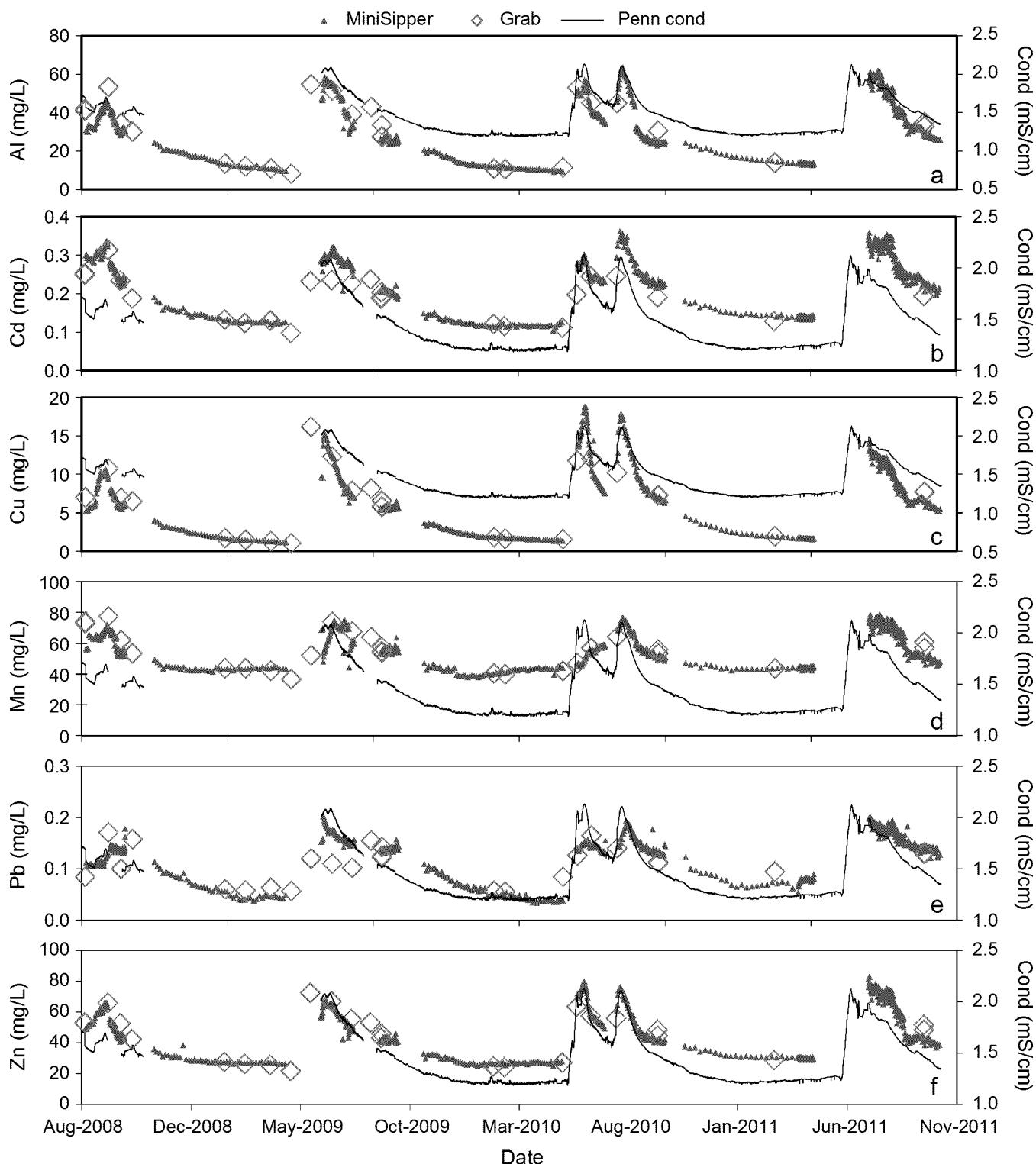


Fig. 4. Pennsylvania Mine MiniSipper metal data for Al (a), Cd (b), Cu (c), Mn (d), Pb (e) and Zn (f) and conductivity from 2008 to 2011 ($n = 750$). The large blue symbols are hand collected EPA or USGS grab samples ($n = 28$).

4. Discussion

4.1. MiniSipper performance

4.1.1. MiniSipper limitations and considerations

The MiniSipper is a new water sampling concept and it is important to discuss the reliability and accuracy of the MiniSipper technology as

well as point out the differences with current water sampling methods. The MiniSipper is an in situ instrument and therefore requires robust mechanical and electronic design to enable the instrument to operate for many months in waters with near freezing temperatures, low pH, and large changes in water flow. MiniSipper reliability and deployment duration have improved as issues of power management, sample preservation, and sample filtration have been resolved but MiniSipper

failures sometimes occurred. Failures were primarily caused by leaking pumps and the MiniSipper will shut down if too much water is in the electronics housing, leading to the data gaps observed in Fig. 4. We have had some difficulty capturing the very beginning of the snow melt runoff signal at the Pennsylvania Mine (Fig. 4) but MiniSipper deployments at other locations have successfully operated for over 8 months under snow and ice.

Developing a low cost, easily portable, battery powered water sampling instrument that can operate for over 8 months unattended requires many design compromises. The MiniSipper can operate under surface ice and snow provided the instrument is in liquid water and not frozen. If the MiniSipper is frozen the micro-pumps will not pump a sample and there is a possibility of sample coil rupture due to expanding ice. The MiniSipper electronics housing is not pressure compensated so the MiniSipper can only be deployed in waters $b \leq 1$ m. Deploying at deeper depths will create pressure gradients that the solenoid micro-pumps are not able to pump against. It would be possible to fill the air spaces in the MiniSipper with an inert oil to create an instrument that can be submerged to greater depths. However, this would greatly increase the expense and difficulty of instrument operation so a 1 m depth limitation was considered acceptable.

The MiniSipper sampling methodology is quite different from other automated water samplers and the QA/QC (quality assurance, quality control) procedures differ from normal water sampling methods. With grab sampling or automated water sampler methods, each water sample is processed with a separate filter and sample container and system blanks are typically determined by passing a blank sample through all the processing steps. In MiniSipper methodology, all the water samples are pulled through a single 10 μm filter and the samples are separated by gas bubbles in one long sample coil so issues of sample carryover become important. Sample carryover is typically $b \leq 0.1\%$ between adjacent samples in the sample coil. However, the effect of pumping 250 segmented samples through the entire sample coil results in a cumulative carryover of 5–10% and represents a system blank rather than an absolute blank. Efforts to minimize the sample carryover focus on improving the reliability of the bubble separation but there is no way to completely eliminate sample carryover in the MiniSipper methodology. A 10% system blank was deemed acceptable for our purposes.

Long-duration MiniSipper deployments can greatly increase sample collection and decrease field sampling costs but analytical costs could quickly consume a researcher's budget. A typical MiniSipper deployment produces 250 water samples which could cost several thousand dollars (USD) for ICP-MS analysis. Analytical costs can be kept in check by using concurrent conductivity and flow data to identify

periods of interest and carefully selecting a subset of MiniSipper samples to analyze.

4.1.2. MiniSipper sample filtration, preservation, and comparison with EPA-USGS grab samples

Samples collected by the MiniSipper have attributes that do not comply with standard EPA sampling methods (EPA Method, 1669). Samples collected by hand or with conventional automated samplers are typically filtered through 0.45 μm filters and this fraction is considered "dissolved". MiniSipper samples are filtered in situ with a 10 μm polyethylene filter and every sample is pulled through the same filter. The high surface area of the 10 μm polyethylene filter resists clogging and these filters have provided effective long duration filtration in waters with very high particle loads. We are working on sequential filtration down to 0.45 μm filtration but have not yet been able to achieve reliable 0.45 μm filtration that can last for an 8 month deployment in particle laden waters.

Another operational difference with MiniSipper sampling is that MiniSipper samples are preserved in situ ($\text{pH} \sim 2$) and stored for up to 8 month in the sample coil. Acid preservation is used to keep particle reactive metals such as Al, Cu, Fe, and Pb in solution but holding times greater than 6 months are generally not recommended by EPA water sampling methodology (EPA Method, 1669). While the MiniSipper results do not comply with standard EPA sample collection methods, the insights gained by the high-resolution, long-duration sampling capabilities of the MiniSipper have not been achieved by any other sampling methodology.

The best reference for evaluating the effectiveness of sample filtration, sample preservation and overall MiniSipper accuracy is to compare metal data from the MiniSipper with metal data from grab samples independently collected and analyzed by EPA and USGS personnel. EPA and USGS sample collection, analysis and QA/QC procedures are considered to be standard methods in water quality monitoring and comparison of MiniSipper and grab sample results provides a robust test of MiniSipper accuracy. Fig. 6 shows the direct comparison between EPA and USGS 0.45 μm filtered grab samples and the closest MiniSipper samples (usually within 24 h, $n = 22$). Our results show that MiniSipper and grab sample results usually agree within 10% for Al, Cd, Cu, Mn, Pb, and Zn (Figs. 4 and 6). MiniSipper results do not agree as closely with the unfiltered 'total' results for particle reactive elements such as Al, Cu and Pb (not shown). Our results indicate that the MiniSipper 10 μm filter provides sample filtration comparable to 0.45 μm grab sample filtration which was our intended goal. Good agreement of MiniSipper and EPA-USGS grab sample results for pH sensitive and particle reactive metals such as Al, Cu and Pb indicates

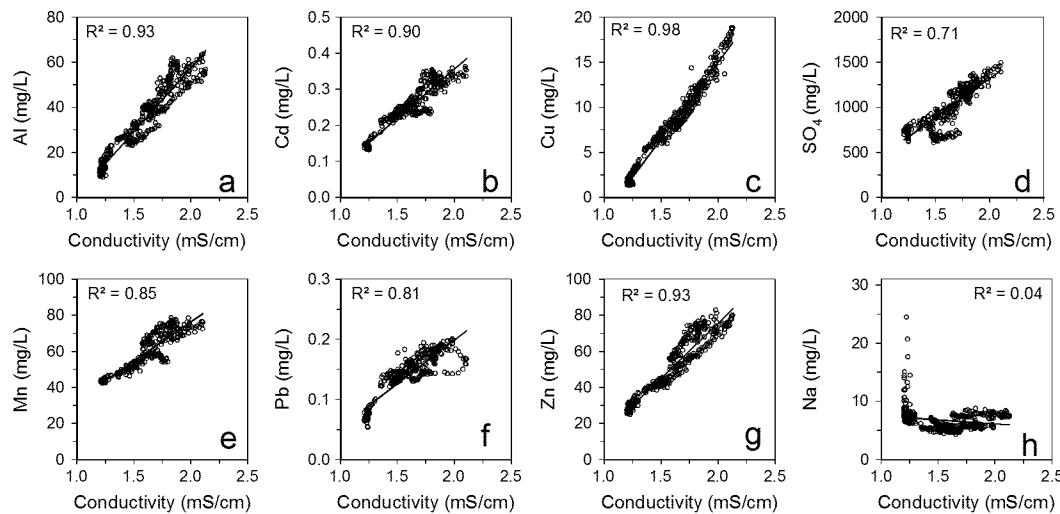


Fig. 5. Element–conductivity correlations for Al (a), Cd (b), Cu (c), SO₄ (d), Mn (e), Pb (f), Zn (g) and Na (h) ($n = 470$).

that our acidification scheme and long sample storage times provide sufficient sample preservation for our purposes (Figs. 4 and 6). The very close agreement between MiniSipper results and EPA-USGS grab sample results also indicates that the potential problem of sample carryover in MiniSipper samples is relatively minor. The fact that our MiniSipper results show excellent agreement with grab samples collected and analyzed independently by EPA and USGS scientists gives very high confidence to the accuracy of the MiniSipper sampling methodology.

4.2. Temporal changes in metal concentrations and loading

4.2.1. Annual metal pattern at the Pennsylvania Mine

Acid mine drainage in runoff dominated mines often shows one of two patterns: 1) a dilution of metal concentrations during runoff (Kimball, 1999; Butler et al., 2008); or 2) a 'first flush' response (Olías et al., 2004; Canovas et al., 2007, 2010; Gyzl and Banks, 2007; Nordstrom, 2009; Davies et al., 2011; Sondergaard et al., 2012). The 'first flush' response occurs after a prolonged dry period when rising mine water levels come into contact with efflorescent mineral salts or isolated mine pools which rapidly increases metal concentrations. The 'first flush' high metal pulse is usually short lived and metal concentrations fall rapidly as further runoff dilutes the metal signal (Nordstrom, 2009; Canovas et al., 2010; Davies et al., 2011). Metal concentrations at the Pennsylvania Mine show neither a dilution minimum nor a 'first flush' signal during snowmelt runoff but instead show a rapid increase followed by a very slow decline over the next few months to low flow winter concentrations. The pattern is very consistent from year to year but can be interrupted by large rain events (Fig. 4).

4.2.2. Rainfall effects at the Pennsylvania Mine

Significant thunderstorms were observed in summer 2010 and led to dramatic changes in water quality flowing out of the Pennsylvania Mine. Fig. 7 shows the Zn concentration, flow and conductivity response to snowmelt runoff during June and large rainstorms at the end of July and beginning of August 2010. During the late summer rainstorm, water flow at the Pennsylvania Mine Level F adit started to increase on August 3, 2010 and conductivity and metal concentrations began to increase within 24 h (Fig. 7). The increase in metal concentrations at the Pennsylvania Mine due to rain events in summer of 2010 was similar to metal increases observed during the snowmelt runoff in June 2010 and has not been documented before (Figs. 4 and 7). Metal concentrations did not quickly decline after the initial metal pulse as would be expected in a 'first flush' response (Nordstrom, 2009). Instead, metal concentrations declined slowly, taking over a month to return to pre-rain metal concentrations

(Fig. 7). Large rain events were not recorded in either 2009 or 2011 and no late summer pulse of high metal waters was observed during these years.

4.2.3. High metal waters at the Pennsylvania Mine

The large increase and slow decline of metal concentrations and water flow observed during both snowmelt runoff and large rain events suggests that a secondary source of high metal water exists within the Pennsylvania mine system (Fig. 4). Our data indicate that there are two basic modes of acid mine drainage outflow at the Pennsylvania Mine, a 'Baseline' flow and a 'High Runoff' flow. During most of the year, 'Baseline' water with metal concentrations and water flows similar to those observed in the late winter drains the Pennsylvania Mine (Figs. 3 and 4). Preliminary data from oxygen and tritium isotopes indicate that water flowing out of the Pennsylvania Mine is not older groundwater but is actually young snowmelt water (M. Wireman, EPA, personal communication). We propose that snowmelt runoff or water from large rainstorms infiltrates the mine workings and comes into contact with efflorescent salts or isolated mine pools which rapidly increases metal concentrations. The increase in the water level within the mine workings then pushes the 'High Runoff' waters into the Pennsylvania Mine outflow and we observe higher flow and higher metal concentrations (Figs. 3 and 4). The slow decline in metal concentrations and water flow implies that the snowmelt or rainfall runoff does not pass quickly through the system and that the subsurface flow paths in the mine are complex (Fig. 4). High metal rain events are not observed every year (2009, 2011) so it appears that there is some water infiltration threshold that must be reached to trigger the high metal flow during rain events (Fig. 7).

4.2.4. Pennsylvania Mine metal loading contribution to the Snake River

An estimate of the Pennsylvania Mine Level F metal loading to the Snake River during specific flow periods in 2010 is presented in Table 1. Metal loading estimates use the observed MiniSipper metal concentrations and flow at the Pennsylvania Mine during low flow (March 3, 2010) peak flow (June 9, 2010), and during a prolonged rainstorm (early August 2010). Metal concentrations for SW-050 and SW-082 were from EPA and USGS grab samples while flow is estimated from the USGS gage station at SW-082. The Pennsylvania Mine metal load percent contributions to SW-050 and SW-082 listed in Table 1 assume no metal losses by adsorption or precipitation during transit to the Snake River and are presented as a relative indicator of the maximum potential metal loading (Table 1).

Stream water changes from pH ~3 at the Pennsylvania Mine to pH 5–7 at SW-050 and pH 6–8 at SW-082 (Table 1). Iron and aluminum colloids form within Peru Creek and concentrations of particle reactive metals such as Al, Cu, Pb, and to some extent Mn, would be expected to decrease markedly due to adsorption as Pennsylvania

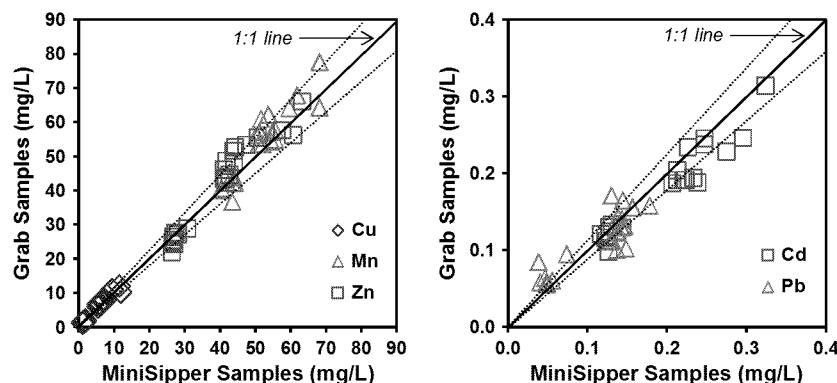


Fig. 6. Direct comparison of MiniSipper and EPA-USGS grab sample 0.45 μm filtered metal results ($n = 22$). Dashed lines above and below 1:1 line represent 10% deviation between MiniSipper and grab sample results.

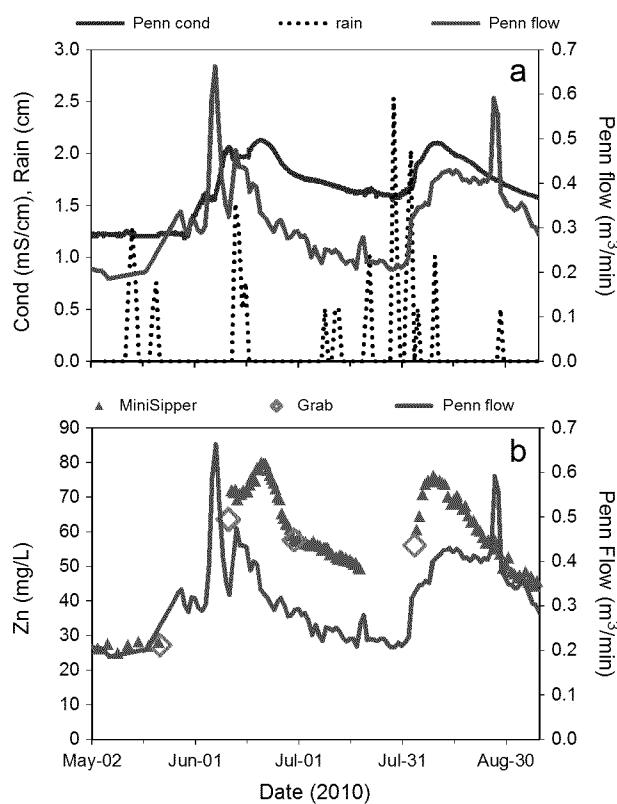


Fig. 7. Effects of snowmelt runoff and rainfall on Pennsylvania Mine flow and conductivity (a). Zn response to flow and conductivity changes at the Pennsylvania Mine. Large symbols are hand collected grab samples (b).

Mine water makes its way into the Snake River (Fey et al., 2002). Adsorption for Cu appears to be the greatest since the Pennsylvania Mine alone could provide over 100% of the total Cu load observed at SW-050 and SW-082 in the Snake River (Table 1). Metals such as Zn and Cd show less partitioning into particulate phases at pH 7 so the potential Pennsylvania Mine contribution of Zn and Cd to SW-050 and SW-082 is more realistic.

The change in the percentage of Pennsylvania Mine potential load contribution to the Snake River during the different flow periods presents some interesting considerations. Metal concentrations at SW-050 and SW-082 display minimum values during snowmelt runoff and maximum values during winter low flow (Table 1; Fey et al., 2002; Todd et al., 2007). During low flow periods, the Pennsylvania Mine potentially contributed 16–60% of the metal load at SW-050 and 14–87% of the metal load at SW-082 (Table 1). During snowmelt runoff in June, 2010, the Pennsylvania Mine metal load increased 3–10 fold over base flow conditions. However, discharge in the Snake River increased 30 fold during snowmelt runoff and greatly diluted any inputs from the Pennsylvania Mine. Excluding Cu, the Pennsylvania Mine could potentially contribute 7–19% of the metal load at SW-050 and SW-082 during snowmelt runoff. Our load estimates also show that during low flow periods the maximum potential metal contribution from the Pennsylvania Mine to SW-050 ranges from about 15–50%, consistent with loading estimates from the Colorado Department of Public Health and Environment TMDL report (CDPHE, 2008).

The impact of the late summer 2010 rainstorm on metal loads to the Snake River was not as dramatic as expected. Metal fluxes from the Pennsylvania Mine increased about 3 fold over low flow conditions during the August rainstorm. However, the rainstorm increased the Snake River flow by 4 fold so the net effect was no change or a slight decrease in metal concentrations at SW-050 and SW-082 during the rain event (Table 1). Excluding Cu, the Pennsylvania Mine potentially contributed 20–30% of the metal load to SW-050 and SW-082 during the August 2010 rainstorm. This is a lower percentage than observed during low flow conditions but higher than observed during snowmelt runoff (Table 1).

These flux estimates emphasize the importance of Pennsylvania Mine toxic metal loading during winter when Snake River metal concentrations are highest and the water flow is lowest (Fey et al., 2002; Todd et al., 2007). Zinc has been identified as the toxic metal of greatest concern in the Snake River and the viability of a Snake River trout fishery is dependent on over-winter survival and over-winter Zn concentrations (Todd et al., 2007). During winter low flow, the Pennsylvania Mine potentially contributes 33–50% of the Zn load observed at SW-050 and SW-082 (Table 1). The highest toxic metal loading from the Pennsylvania Mine occurs during snowmelt runoff but the downstream effects are minimized by watershed dilution and the snowmelt runoff period does not pose the greatest threat to a Snake River trout

Table 1
Pennsylvania Mine metal loading during low flow, peak flow, and rainstorm flow in 2010. The Pennsylvania Mine percent metal load contributions to SW-050 and SW-082 assume no adsorption or precipitation during transit to the Snake River and are presented as a relative indicator of potential metal loading.

	Flow (L/s)	pH	Cd (mg/L)	Cu (mg/L)	Mn (mg/L)	Pb (mg/L)	Zn (mg/L)	Cd (kg/d)	Cu (kg/d)	Mn (kg/d)	Pb (kg/d)	Zn (kg/d)
Low flow (Mar 3, 2010)												
Penn Mine	4	4.4	0.122	1.83	40.7	0.05	27.2	0.04	0.6	14	0.02	9
SW-050	210	6.4	0.006	0.07	1.87	0.006	1.55	0.11	1.3	34	0.11	28
SW-082	280	6.2	0.003	0.03	0.70	0.005	0.70	0.07	0.7	17	0.12	17
% Penn Load at SW-050							39%	50%	41%	16%	33%	
% Penn Load at SW-082							58%	87%	83%	14%	56%	
Peak flow (June 7, 2010)												
Penn Mine	11	2.9	0.30	19	500	0.15	80	0.29	18.1	48	0.14	76
SW-050	12170	6.7	0.002	0.011	0.640	b.001	0.54	2.10	11.5	672	1.05	567
SW-082	18700	6.5	0.001	0.009	0.285	b.001	0.25	1.62	14.5	452	1.62	404
% Penn Load at SW-050							14%	156%	7%	14%	13%	
% Penn Load at SW-082							18%	124%	11%	9%	19%	
Rain event (Aug 9, 2010)												
Penn Mine	7	2.9	0.360	18	75	0.19	76	0.22	10.9	45	0.11	46
SW-050	1700	5.1	0.006	0.09	1.46	0.004	1.35	0.88	13.2	214	0.59	198
SW-082	2600	6.9	0.003	0.03	0.70	0.004	0.70	0.67	6.7	157	0.90	157
% Penn Load at SW-050							25%	82%	21%	20%	23%	
% Penn Load at SW-082							32%	162%	29%	13%	29%	

Table 2

MiniSipper Baseline, High Runoff, and total annual metal loading estimates during 2010 and CDPHE (2008) annual loading estimates for the Pennsylvania Mine. MiniSipper metal loading was calculated from daily flow and metal concentrations. Metal concentrations were estimated from metal-conductivity correlations during the periods when no MiniSipper metal data was available (60 out of 365 days). MiniSipper loading estimates are only for surface water flow out of the Level F adit while the CDPHE annual loading estimates include surface and subsurface flows from the entire Pennsylvania Mine area.

	Average flow (m ³ /min)	Cd (kg/y)	Cu (kg/y)	Mn (kg/y)	Pb (kg/y)	Zn (kg/y)
MiniSipper total annual load	0.29	28	860	7900	16	6000
MiniSipper Baseline annual load	0.25	17	225	5900	10	3570
MiniSipper High Runoff annual load (total load - baseline load)		11	635	200	6	2430
MiniSipper Baseline contribution to total annual loading		61%	26%	75%	63%	60%
Pennsylvania Mine annual loading estimates (CDPHE TMDL, 2008)	0.54	85	2044	9786	10	17,680

fishery (Todd et al., 2007). Remediation efforts focused on reducing the metal loading at the Pennsylvania Mine during the winter low flow period and not the snowmelt runoff period could greatly enhance the viability of a year round trout fishery.

4.2.5. Pennsylvania Mine conductivity derived annual loading estimates

Specific conductivity–metal correlations for Cd, Cu, and Zn were very high ($R^2 > 0.9$) at the Pennsylvania Mine (Fig. 5). Lead and manganese have slightly lower correlations with specific conductivity, $R^2 \sim 0.8$ most likely due to the pH adsorption effects and the pyrite mineralogy at this site. The high metal–conductivity correlations can allow conductivity to be used as a proxy for metal concentrations during periods when no metal data are available (Canovas et al., 2010). For 2010, we have MiniSipper metal data covering 305 out of 365 days and can use conductivity estimated metal concentrations to fill in the missing 60 days.

Fig. 8 shows the measured Zn flux calculated from actual MiniSipper Zn concentrations and flow data and the Zn flux estimated from the conductivity–Zn correlation and flow data. As expected, the high correlation of Zn and specific conductivity results in very close agreement between observed Zn flux and the conductivity estimated Zn flux (Fig. 8). During 2010, the Zn flux increased 5 fold in response to snowmelt runoff in June. The increase in Zn flux was due to a 2.5 fold increase in Zn concentrations and a two fold increase in water flow (Fig. 8). Zinc flux decreased during July 2010 but increased again in August 2010 in response to the prolonged rainstorm. The magnitude of the rainstorm Zn flux was about the same as the snowmelt runoff Zn flux. A sharp Zn flux spike was observed in late August and this was caused by a flow spike and not a Zn concentration spike (Figs. 7 and 8).

With year round MiniSipper metal data, flow data, and conductivity estimated metal concentrations from periods without data, we can more accurately calculate total annual metal loads for water year 2010 (Table 2). The Pennsylvania Mine ‘Baseline’ metal annual load is

the average winter low flow metal concentration multiplied by the winter water flow and summed for 365 days. The ‘High Runoff’ load is the difference between the total annual metal load and the ‘Baseline’ annual load and represents the metal load that may be attributed to the ‘High Runoff’ loading events, either snowmelt runoff or rainstorms.

Our MiniSipper loading results indicate that over 60% of the annual load of Cd, Mn, Pb, and Zn and 25% of the annual load of Cu from the Pennsylvania Mine could be attributed to the low flow ‘Baseline’ load. The metal loading estimates calculated for Table 1 demonstrate that while runoff events greatly increase metal loading from the Pennsylvania Mine, watershed dilution minimizes the effect downstream in the Snake River. Any remediation effort is expensive so EPA is seeking the most cost effective approach to reducing metal inputs from the Pennsylvania Mine. If a source area and/or mechanism for the Baseline waters can be identified then effective remediation efforts could significantly reduce Pennsylvania Mine metal loading to Peru Creek and the Snake River (Table 2). Reducing the Baseline loading during low flow periods would have the greatest impact on aquatic life downstream since the low flow periods in late summer and over-winter are the times when aquatic life is most severely stressed by metal pollution (Todd et al., 2007). Annual metal loads from Table 2 and instantaneous metal loads from Table 1 provide further confirmation that the winter low flow period is the time when the Pennsylvania Mine has the maximum effect on the Snake River watershed.

Most TMDL and annual element loading estimates are made with very few element concentration and flow data points. The CDPHE TMDL loading estimates for the Pennsylvania Mine were calculated with one measured flow rate (0.54 m³/min), an average of monthly metal concentration estimates, and included subsurface flows from the entire mine site (Table 2, CDPHE, 2008). MiniSipper loading estimates for Cd, Cu and Zn are about a third of the CDPHE TMDL estimates but are not directly comparable since the CDPHE estimate includes subsurface metal inputs as well as the Level F input

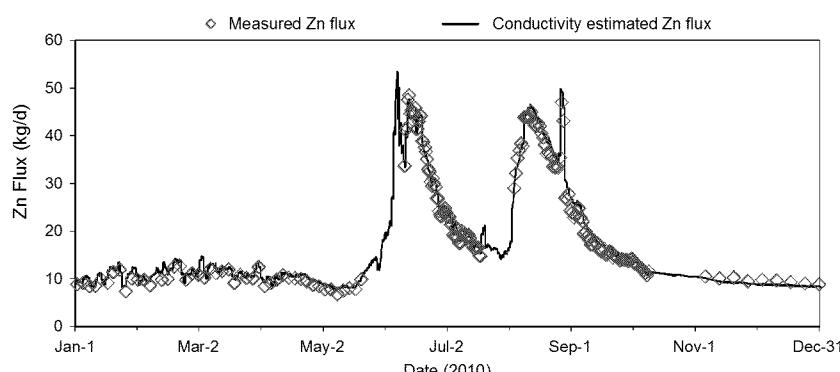


Fig. 8. Measured Zn load and Zn load estimated from conductivity at the Pennsylvania Mine during 2010.

(Table 2). We would argue that our high resolution metal and flow data provide a more accurate estimate of the metal loading from the Pennsylvania Mine.

4.2.6. Potential real-time metal load estimates

At locations where metals are highly correlated with conductivity, the use of real-time flow and conductivity data can provide real-time estimates of metal loads. Using the MiniSipper to collect water samples year round, especially during times of major hydrologic events, would provide the water sampling data necessary to establish robust metal-conductivity relationships. Once a robust metal-conductivity relationship is established, a combination of real-time conductivity and flow telemetry would provide real-time metal flux estimates. A low resolution MiniSipper sampling strategy at key times of the year would be necessary to monitor any variations in metal-conductivity relationships but this low resolution sampling would be relatively inexpensive. Instrumentation for real-time monitoring of flow and conductivity is well established, capable of winter operation in remote areas, and relatively inexpensive. The use of in situ flow and conductivity monitoring could provide real-time metal estimates for relatively low cost and we are hoping to develop real-time metal flux monitoring at the Pennsylvania Mine.

5. Conclusions and future applications

MiniSippers have provided nearly continuous toxic metal sampling coverage at the Pennsylvania Mine site since late 2008. MiniSipper metal data show excellent agreement with hand collected EPA and USGS grab samples, usually within 10%. In contrast to many acid mine drainage systems, the Pennsylvania Mine shows greatly elevated metal concentrations during snowmelt runoff and, in some years, after prolonged precipitation events. High correlations between toxic metals and conductivity at the Pennsylvania Mine allow the use of conductivity as a proxy for metal concentrations and more realistic estimates of annual metal loading at low cost.

We initially developed the MiniSipper for monitoring surface acid mine drainage waters but MiniSippers have also been used for: 1) long-term monitoring of deep underground acid mine drainage systems; 2) high resolution sampling during tracer injection studies, both surface waters and deep underground; 3) long-term, high-resolution metal monitoring of watersheds impacted by wildfires; and 4) high resolution sampling for diel metal cycling studies. New MiniSipper instruments undergoing field testing include the Event Response MiniSipper and the Borehole MiniSipper. Rain events are very difficult to sample in remote areas so the Event Response MiniSipper is designed to collect samples at low frequency (i.e. daily) during normal operation but can change to high frequency sampling (i.e. hourly) during a rain triggered event. With over 250 samples available, a number of storm events could be sampled during a multi-month deployment. The Borehole MiniSipper fits down a 5 cm monitoring well, collects 50 groundwater samples, and has been deployed for year round monitoring of groundwater in a watershed impacted acid mine drainage.

MiniSipper sampling technology is very versatile and has proven capable of providing high quality, high-resolution data in many diverse applications. MiniSippers have primarily been applied to metal monitoring but MiniSipper sampling technology could potentially be used for other analytes of interest such as pesticides, nutrients, pharmaceuticals, etc. Compared to standard automated water samplers, the MiniSipper design: 1) increases sampling capacity by over 10 fold; 2) increases deployment duration by over 10 fold; 3) allows for easier deployment in remote areas difficult or dangerous to access sites; and 4) greatly reduces site visits and field sampling costs.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2012.07.083>.

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